Sertifikaat

PATENTKANTOOR
REPUBLIC OF SOUTH AFRICA

DEPARTEMENT VAN HANDEL
EN NYWERHEID

Certificate

PATENT OFFICE
REPUBLIEK VAN SUID-AFRIKA

DEPARTMENT OF TRADE AND
INDUSTRY

Hiermee word gesertifiseer dat
This is to certify that

1) South African Patent Application No. **2002/5387** accompanied by a Provisional Specification was filed at the South African Patent Office on **5 July 2002** in the name of **Sasol Technology (Pty) Ltd** in respect of an invention entitled: **"Phosphine Ligands metathesis catalysts and catalysts including such Ligands"**

2) The Photocopy attached hereto is a true copy of the provisional specification filed with South African Patent Application No. **2002/5387.**

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

Geteken te / Signed at PRETORIA in die Republiek van Suid-Afrika, hierdie / in the Republic of South Africa, this **2nd** dag van / day of **July 2002**

Registrateur van Patente

Form P1

REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

REGISTER OF PATENTS

OFFICIAL APPLICATION NO.	LODGING DATE : PROVISIONAL	ACCEPTANCE DATE
21 01 2002/5361	22 5 July 2002	43
INTERNATIONAL CLASSIFICATION	LODGING DATE : COMPLETE	GRANTED DATE
51	23	

FULL NAME(S) OF APPLICANT(S) / PATENTEE(S)

71 SASOL TECHNOLOGY (PTY) LTD

APPLICANTS SUBSTITUTED :	DATE REGISTERED
71	

ASSIGNEE(S)	DATE REGISTERED
71	

FULL NAME(S) OF INVENTOR(S)

72 DWYER, Catherine Lynn

PRIORITY CLAIMED	COUNTRY	NUMBER	DATE
N.B. Use international abbreviation for country. (See Schedule 4)	33	31	32

TITLE OF INVENTION

54 PHOSPHINE LIGANDS FOR METATHESIS CATALYSTS AND CATALYSTS INCLUDING SUCH LIGANDS

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ADDRESS FOR SERVICE	REF
74 D M Kisch Inc, 66 Wierda Road East, Wierda Valley, SANDTON	P24751ZA00

PATENT OF ADDITION NO.	DATE OF ANY CHANGE
61	

FRESH APPLICATION BASED ON	DATE OF ANY CHANGE

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

-5.7.02 INKOMSTE DEPT

Form P.1
PDHR 229
REPUBLIEK VAN SUID-AFRIKA

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT
(Section 30 (1) - Regulation 22)
The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate.

OFFICIAL APPLICATION NO		
21	01	2002/5307

DMK REFERENCE
P24751ZA00

FULL NAME(S) OF APPLICANT(S)

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TITLE OF INVENTION

54 PHOSPHINE LIGANDS FOR METATHESIS CATALYSTS AND CATALYSTS INCLUDING SUCH LIGANDS

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANING FORM P2
The earliest priority claimed is

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.	21	01	
THIS APPLICATION IS FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.	21	01	

THIS APPLICATION IS ACCOMPANIED BY :

x	1a	A single copy of a provisional specification of 12 pages.
	1b	Two copies of a complete specification of pages.
	2a	Informal drawings of sheets.
	2b	Formal drawings of sheets.
	3	Publication particulars and abstract (form P8 in duplicate).
	4	A copy of figure of the drawings for the abstract.
	5	Assignment of invention (from the inventors) or other evidence of title.
	6	Certfied priority document(s).
	7	Translation of priority document(s).
	8	Assignment of priority rights.
	9	A copy of form P2 and a specification of S.A. Patent Application. 21 01
	10	A declaration and power of attorney on form P3.
	11	Request for ante-dating on form P4.
	12	Request for classification on form P9.
	13a	Request for delay of acceptance on form P4.
	13b	

DATED 5 July 2002

Patent Attorney for Applicant(s)

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RECEIVED
OFFICIAL DATE STAMP
REGISTRAR OF PATENTS

The duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with official stamp.

D. M. Kisch Inc, Sandton

Form P.6

REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

PROVISIONAL SPECIFICATION
(Section 30 (1) - Regulation 27)

OFFICIAL APPLICATION NO.		LODGING DATE		DMK REFERENCE
21	01 2002/5361	22	5 July 2002	P24751ZA00

FULL NAME(S) OF APPLICANT(S)	
71	SASOL TECHNOLOGY (PTY) LTD

FULL NAME(S) OF INVENTOR(S)	
72	DWYER, Catherine Lynn

TITLE OF INVENTION	
54	PHOSPHINE LIGANDS FOR METATHESIS CATALYSTS AND CATALYSTS INCLUDING SUCH LIGANDS

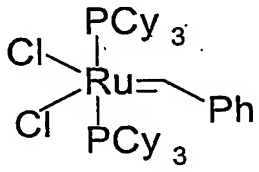
Technical Field

The invention relates to the use of a phosphine ligand for producing a homogeneous metathesis catalyst, for example a Grubbs catalyst. The invention also relates to a homogeneous metathesis catalyst including such a phosphine ligand and to a metathesis process using the catalyst.

Background to the invention

A great deal of research has been done in an attempt to synthesize and isolate catalysts which are able to catalyze homogeneous olefin metathesis reactions. More particularly the synthesis of Group VIII transition metal metathesis catalysts has lead to catalysts with increased functional group tolerance and stability with respect to conditions such as air, water and acids.

During the 1990's the so-called "Grubbs catalyst" of formula 1 was developed:



.....(1)

where C_y is cyclohexyl.

This ruthenium (Ru) based catalyst afforded high selectivities, high reaction rates and good tolerance for oxygenates in feed during homogeneous olefin metathesis reactions.

Although much research has been carried out to investigate the effect of changing the nature of the ligands, the main thrust of second generation Grubbs catalysts research has related to a move away from the use of phosphine ligands to the use of highly nucleophilic carbenes for homogeneous metathesis reactions.

In the case of hydroformylation reactions, research has continued into the use of phosphine ligands. It will be appreciated that in a hydroformylation process an olefinic feedstock is reacted with carbon monoxide and hydrogen at elevated temperatures and pressures in the presence of a hydroformylation catalyst to produce oxygenated products. The hydroformylation catalyst is selected according to the particular oxygenated products which are required from a particular olefinic feedstock and may typically be phosphine and/or phosphite ligand modified rhodium (Rh) or cobalt (Co) homogeneous catalyst. However, research into hydroformylation reactions has indicated that those phosphine ligands which appeared to lead to catalysts with higher selectivities and reaction rates in homogeneous metathesis reactions were often not suitable for the types of catalysts used in hydroformylation reactions, for example $Co(CO)_3P$ where P represents a phosphine ligand, for example tricyclohexyl phosphine (PCy_3).

However, it has now surprisingly been found that phosphabicylononane ligands, which are generally used in hydroformylation reactions, provide excellent stability, product yields and selectivities when used in a homogeneous

metathesis catalyst.

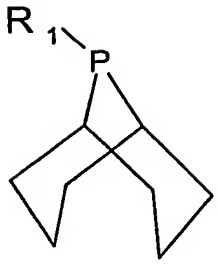
Summary of the invention

According to a first aspect of the present invention there is provided a homogeneous metathesis catalyst which includes a phosphine ligand characterized therein that the phosphine ligand is a heterocyclic structure wherein at least one hetero-atom is phosphorous.

According to a second aspect of the invention there is provided the use of a phosphine ligand in a homogeneous metathesis catalysed reaction wherein the phosphine ligand is a heterocyclic structure with at least one hetero-atom being phosphorous.

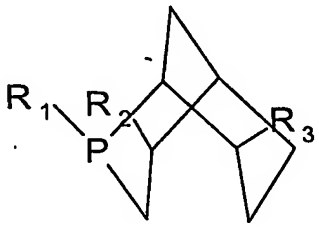
The phosphine ligand may be a substituted or unsubstituted monophosphacycloalkane.

Particularly, the phosphine ligand may be a substituted or unsubstituted bicyclic tertiary phosphine having two cyclic structures and a ligating phosphorus atom. In one form of the invention, the phosphine ligand may be a phosphabicyclononane wherein the ligating phosphorous atom may be located in a bridge linkage position, as indicated in formula 2.



..... (2)

In another form of the invention, the phosphine ligand may be a phosphabicyclononane with the ligating phosphorous atom being neither in a bridgehead position nor a member of a bridge linkage, as indicated in formulas 3 and 4.



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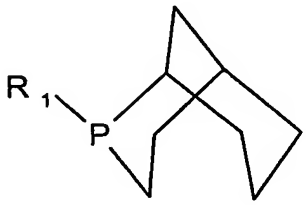

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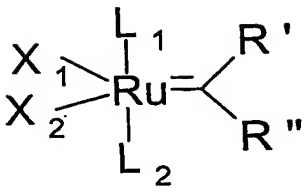
The homogeneous metathesis catalyst may be a Grubbs catalyst of formula 5:



.....(5)

wherein L_1 may be any neutral phosphine or carbene ligand;

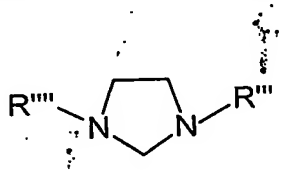
L_2 may be any heterocyclic phosphine ligand;

X_1 and X_2 may be any anionic ligand and may be two different ligands or the same ligand; and

R' and R'' may be different or the same and may be H or organyl.

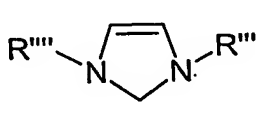
In one embodiment of the invention L_1 may be any neutral phosphine ligand including a heterocyclic phosphine ligand and accordingly may be the same as L_2.

In another embodiment of the invention L_1 may be selected from a group of heterocyclic compounds containing substituted or unsubstituted five membered rings which may be saturated or unsaturated and which may include at least two adjacent or non adjacent nitrogen atoms as part of the group. Examples of such ligands are illustrated as formulas 6, 7 and 8:



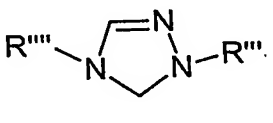
(6)

or



(7)

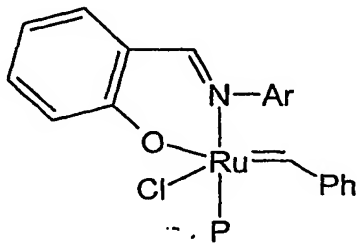
or



(8)

wherein R''' and R'''' may be any group such as alkyl, aryl, cycloalkyl, adamantyl or the like, and may be further substituted with functional groups.

X_1 and X_2 may be any halogen, an oxygen based anionic substituent wherein the oxygen atom is bound directly to the Ru atom, e.g. $R\text{-}O^-$ or $R\text{-}COO^-$ or may be a chelate structure. In one form of the invention, X_1 and L_1 may be linked to form bidentate Schiff base ligands, e.g. as shown in formula 9.



.....(9)

R' and R'' may independently be H, alkyl, aryl or substituted alkyl or aryl. R' and R'' may also be linked to form a bridging connection. In one embodiment of the invention R' may be H and R'' may be any vinylic group. In another embodiment of the invention, R'' may be any phenyl group.

According to another aspect of the invention there is provided the use of a catalyst of formula 5 above in a homogeneous metathesis reaction.

The reaction is preferably a homogeneous metathesis reaction of olefins and the reaction conditions for the metathesis reaction wherein the catalyst of formula 5 is used may be in accordance to conditions which are well known to a person

skilled in the art of metathesis reactions.

According to a further aspect of the invention there is provided a product produced by a homogeneous metathesis reaction using a catalyst substantially as described hereinabove.

The homogeneous metathesis catalyst may be a Grubbs catalyst of formula 5 hereinbefore.

According to yet a further aspect of the invention there is provided a process for a homogeneous metathesis reaction in the presence of a catalyst of the type described hereinbefore.

The process may further be characterized therein that the catalyst is formed in situ. The process may then include the steps of adding together sufficient quantities of a Ruthenium source, which may be an inorganic salt of Ruthenium e.g. $RuCl_3.xH_2O$, a cyclical phosphine ligand, a precursor which would form the carbine structure on the central Ru atom for example an alkyne like butynedioldiacetate and a requisite starting material for the metathesis reaction.

Specific embodiment of the invention

Without limiting the scope thereof, the invention will now be further described with reference to the following examples.

These examples are for metathesis of 1-octene to form 7-tetradecene using an *in situ* catalyst system with a ruthenium concentration of 100ppm. The comparison is between eicosyl phoban (EP) and PCy_3 [the ligand employed in the standard Grubbs catalyst (formula 1)].

General experimental procedure:

Reactions were carried out in a 100 ml three-necked flask fitted with a reflux condenser, thermometer and septum. The reflux condenser was connected to a cooling bath to ensure a constant flow of chilled water through the jacket, thereby preventing loss of octene. The top of the condenser was connected to a cold trap and bubbler in order to monitor liquid losses and gas emissions. The thermometer was positioned below the level of the reaction solution to ensure correct temperature monitoring. The reaction flask was purged with argon to ensure removal of oxygen. The reagents [EP or PCy_3, $RuCl_3.xH_2O$ and 1,4-butynedioldiacetate (BDD)] were added to the flask under inert conditions, then a slow hydrogen sparge was started and maintained during the reaction, and the reaction mixture was heated, with stirring, to the desired temperature. Samples were taken at regular intervals with a syringe through the septum, quenched with a mixture of toluene and two drops of *t*-butylhydroperoxide. Samples were analyzed by GC using a Poha column. Unless otherwise stated, 20 ml of octene was employed in all experiments, and catalyst, solvent and additive amounts were calculated relative to this. 0.5 ml of octadecane was used as internal standard.

A) Comparison of EP and PCy_3 at 50°C

It is evident from the graph that EP performs far better than PCy_3 at 50°C, affording higher reaction rates and conversions. The thermal barrier to catalyst activation is presumably reduced when employing EP as ligand.

Reaction conditions:

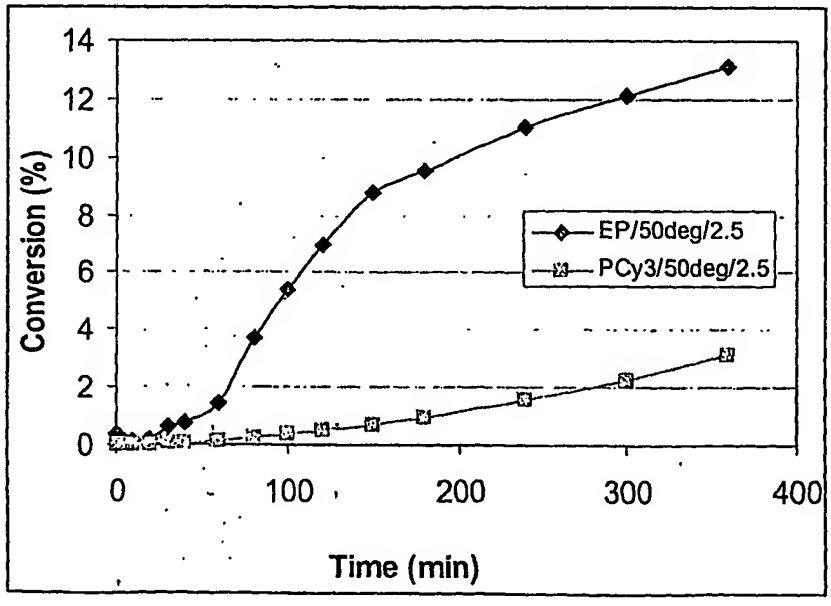
100 ppm Ru

2.5:1 phosphine:ruthenium ratio

10:1 BDD:Ru

T = 50°C

RESULTS:



B) Comparison of EP and PCy_3 at 110°C

At high temperatures, EP shows more sustained catalyst activity, and affords higher yields at lower ligand concentrations (1.5:1 for EP versus 2.5:1 with PCy_3).

Reaction conditions:

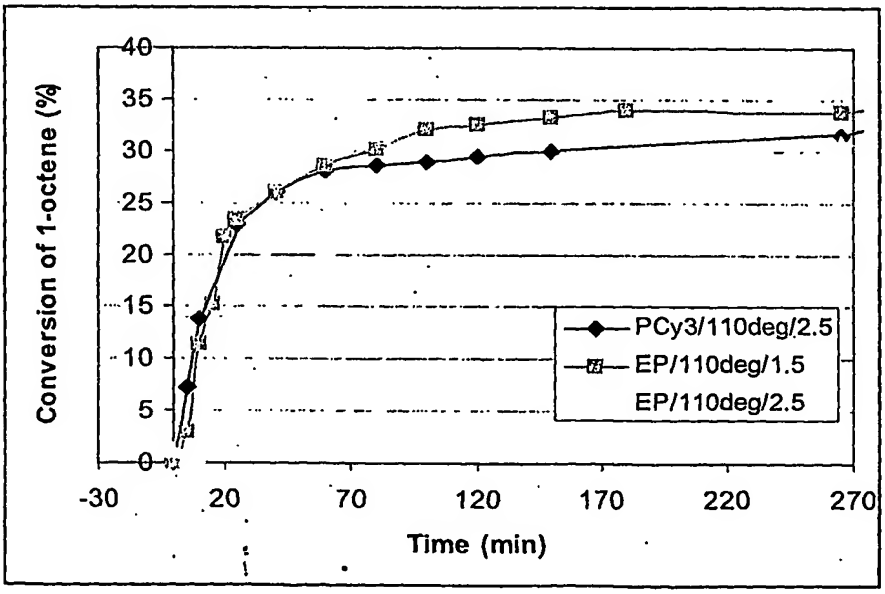
100 ppm Ru

2.5:1 and 1.5:1 phosphine:ruthenium ratio

10:1 BDD:Ru

T = 110°C

RESULTS:



At higher temperatures with a 2:1 ratio of phosphine to ruthenium, PCy_3 affords improved reaction rates, while the corresponding EP reaction is slower. However EP catalyst stability is sustained over a far longer period, and the end of run

conversions are the same for both. This suggests that EP coordinates more strongly to the metal center, thereby giving added catalyst stability but slowing reaction rates as phosphine dissociation is hindered. [According to the generally accepted reaction mechanism, phosphine dissociation is required before metathesis can proceed].

In order to further explore this, less ligand was added (L:M = 1.5:1). In the case of PCy_3 lower ligand concentrations led to poorer yields of the desired metathesis product, presumably due to lower catalyst stabilities. However in the case of EP, lower ligand concentrations afforded improved reaction rates and yields. Thus at 110°C, only 1.5 equivalents of EP are required to get similar reaction rates and improved yields of desired product relative to those obtained with 2.5 equivalents of PCy_3. The reduced amount of ligand required allows a tremendous reduction in process costs.

It will be appreciated that many variations in detail are possible without thereby departing from the spirit and scope of the invention.

Dated this 5 day of July 2002

Patent Attorney / Agent for the Applicant